

OFF-TARGET MOVEMENT OF ENDOSULFAN FROM ARTICHOKE FIELDS IN MONTEREY COUNTY

By

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EXECUTIVE SUMMARY
of Report EH 91-5 Entitled
"Off-Target Movement of Endosulfan from
Artichoke Fields in Monterey County"

Environmental Monitoring and Pest Management Branch
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Protection and Worker Safety
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PURPOSE:

The Environmental Hazards Assessment Program (EHAP) monitored three artichoke fields in the Moss Landing drainage area of Monterey County to determine whether endosulfan moves off-target via spray drift and/or rain runoff. This information will be used to develop mitigation measures to reduce off site movement of endosulfan.

BACKGROUND

Endosulfan is a chlorinated hydrocarbon used as a broad spectrum insecticide on a variety of crops in California. Both the parent compound and endosulfan sulfate, the primary degradation product of environmental concern, are relatively stable in the environment and are highly toxic to fish and other aquatic organisms.

Since 1979, endosulfan residues have consistently been detected in bivalve aquatic organisms in Elkhorn Slough, a state ecological reserve in Monterey County. Historically, some of the highest use of endosulfan in California occurs in Monterey County with the majority of this use on artichokes in the Moss Landing drainage area. Runoff from this drainage area is transported to the mouth of Elkhorn Slough where tidal action moves it into and out of the Slough.

In a previous study, results of soil and sediment sampling for endosulfan residues indicated that areas in the Moss Landing drainage area associated with high endosulfan use are a potential source of the residues found in Elkhorn Slough. However, there is little information on how endosulfan moves off site in these areas, whether it be via drift during application or through runoff water.

STUDY METHODS

Three artichoke fields in the Moss Landing drainage area were monitored in this study. Each field was treated in November of 1988 with a liquid mixture of endosulfan and mevinphos which was applied by helicopter.

The deposition of endosulfan on- and off-target was measured using paper fallout sheets. Off-target fallout sheets were placed around each field at approximately 18 feet from the field borders. Soil

samples were collected from each field and from adjacent collector drains, prior to and immediately following application. Collector drains were dry at the time of soil sampling. Rain runoff samples were collected approximately one week after application in field one, and five weeks after application in all three fields.

RESULTS

Deposition

An average of 1.01 lbs/acre was applied to the three fields, close to the intended rate of 0.94 lbs/acre. Endosulfan residues were detected off-target at all three fields, the average deposition ranging from 0.4 to 1.8% of the intended application rate, and 0.5 to 2.0% of measured rates.

Soil Concentrations

Post-application concentrations in soil taken from collector drains of two fields were slightly larger than pre-application concentrations indicating that some material drifted off-target during application. Post-application concentrations in the collector drain of the third field were about the same as pre-application concentrations indicating that there was no drift or, more likely, that deposition from drift was diluted below measurable levels due to higher wind speeds recorded at the third field during application.

Rain Runoff

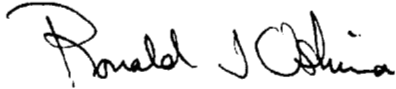
Endosulfan residues were detected in rain runoff from all three fields. Concentrations of endosulfan ranged from 2.2 to 13 $\mu\text{g/L}$, well above the Environmental Protection Agency (EPA) instantaneous water quality criterion of 0.22 $\mu\text{g/L}$ for protection of freshwater organisms. Without sufficient dilution, coupled with multiple sources in a single watershed, these runoff concentrations could adversely affect water quality.

CONCLUSIONS

Results from this study indicate that endosulfan moves off-target via drift and rain runoff from artichoke fields sampled in the Moss Landing drainage area. However, the relative magnitude of drift and runoff losses depends on a variety of environmental parameters including atmospheric conditions, soil type and texture, precipitation patterns, and cultural practices. Even though the relative contribution of these two transport mechanisms was not determined, the study does demonstrate that endosulfan moves off-target in both spray drift and in rain runoff in Monterey County.

Currently, the California Department of Food and Agriculture (CDFA) recommends that permits for endosulfan use not be issued where runoff due to irrigation or rainfall may flow into surface waters.

This recommendation applies to nine counties in California, including Monterey, where there are indications that EPA water quality criteria for endosulfan have been exceeded. However, other counties are also adopting this recommendation. In addition, when endosulfan permits are issued, the CDFA recommends that permits be conditioned to require specific measures to minimize off-site movement due to drift.

A handwritten signature in dark ink, appearing to read "Ronald J. Oshima". The signature is fluid and cursive, with the first name "Ronald" being more prominent.

Ronald J. Oshima
Branch Chief

6/27/91

ABSTRACT

This study was conducted in the Moss Landing drainage area of Monterey County to determine if endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide) moves off-target via spray drift and/or rain runoff from artichoke fields. An average of 1.13 kg/ha of endosulfan (isomers I plus II) was applied to three artichoke fields, close to the intended rate of 1.05 kg/ha. Off-target deposition, 5.5 m from field borders, averaged between 0.005 and 0.019 kg/ha, indicating endosulfan was lost via spray drift during application. Concentrations of total endosulfan in rain runoff ranged from 2.2 to 13 ug/L, indicating this was an additional mechanism for off-target movement. The relative magnitude of these two mechanisms is likely to be dependent on meteorological conditions during and after application in addition to field characteristics. On site, total endosulfan concentrations (I plus II plus sulfate) in soil averaged 1548 and 2962 ug/kg, pre- and post-application, respectively. These concentrations are on the same order of magnitude as other study results from this region.

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DISCLAIMER

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such product.

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INTRODUCTION

Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide) is a chlorinated hydrocarbon used as a broad spectrum insecticide. Technical grade endosulfan is roughly a 2:1 mixture of two stereoisomers commonly designated endosulfan I and II. The primary degradation product of environmental concern is endosulfan sulfate, which is generally more stable in the environment and has similar toxicological properties as the parent compound (Ali et al., 1984).

Endosulfan is considered to be highly toxic to fish and other aquatic organisms (Ali et al., 1984). The United States Fish and Wildlife Service has put endosulfan in its most lethal category, "supertoxic", reserved for compounds having an LC50 below 0.01 mg/L for rainbow trout (U.S. Fish and Wildlife Service 1984). Some LC50 values for fish species range from 0.011 to 3.0 ug/L (Verschueren 1983). In order to protect aquatic organisms, the United States Environmental Protection Agency (U.S. EPA) has established relatively low water quality criteria for total endosulfan (I + II + sulfate). For freshwater organisms, the criteria are 0.056 and 0.22 ug/L for a 24-hour average and instantaneous maximum, respectively (U.S. EPA 1986). Criteria for the protection of saltwater organisms are 0.0087 and 0.034 ug/L for a 24-hour average and instantaneous maximum, respectively (U.S. EPA 1986). These criteria have also been adopted by the California State Water Resources Control Board for the protection of aquatic life in all surface waters of the state (SWRCB, 1990).

Historically, some of the highest use of endosulfan in California occurs in Monterey County (CDFA 1981 - 1988). Endosulfan is used in Monterey on approximately 16 commodities with the majority of this usage on artichokes in the Moss Landing drainage area. This area is a highly productive agricultural region networked with drains and sloughs that channel freshwater runoff to the mouth of Elkhorn Slough and Monterey Bay (Figure 1). Agricultural runoff carrying a variety of pesticides from Blanco Drain, Salinas and Old Salinas Rivers, Moro Cojo, Tembladero, Alisal, and Reclamation Sloughs (Figure 1) is of particular concern since it may be transported into Elkhorn Slough where a state ecological reserve is located (ABA Consultants 1987).

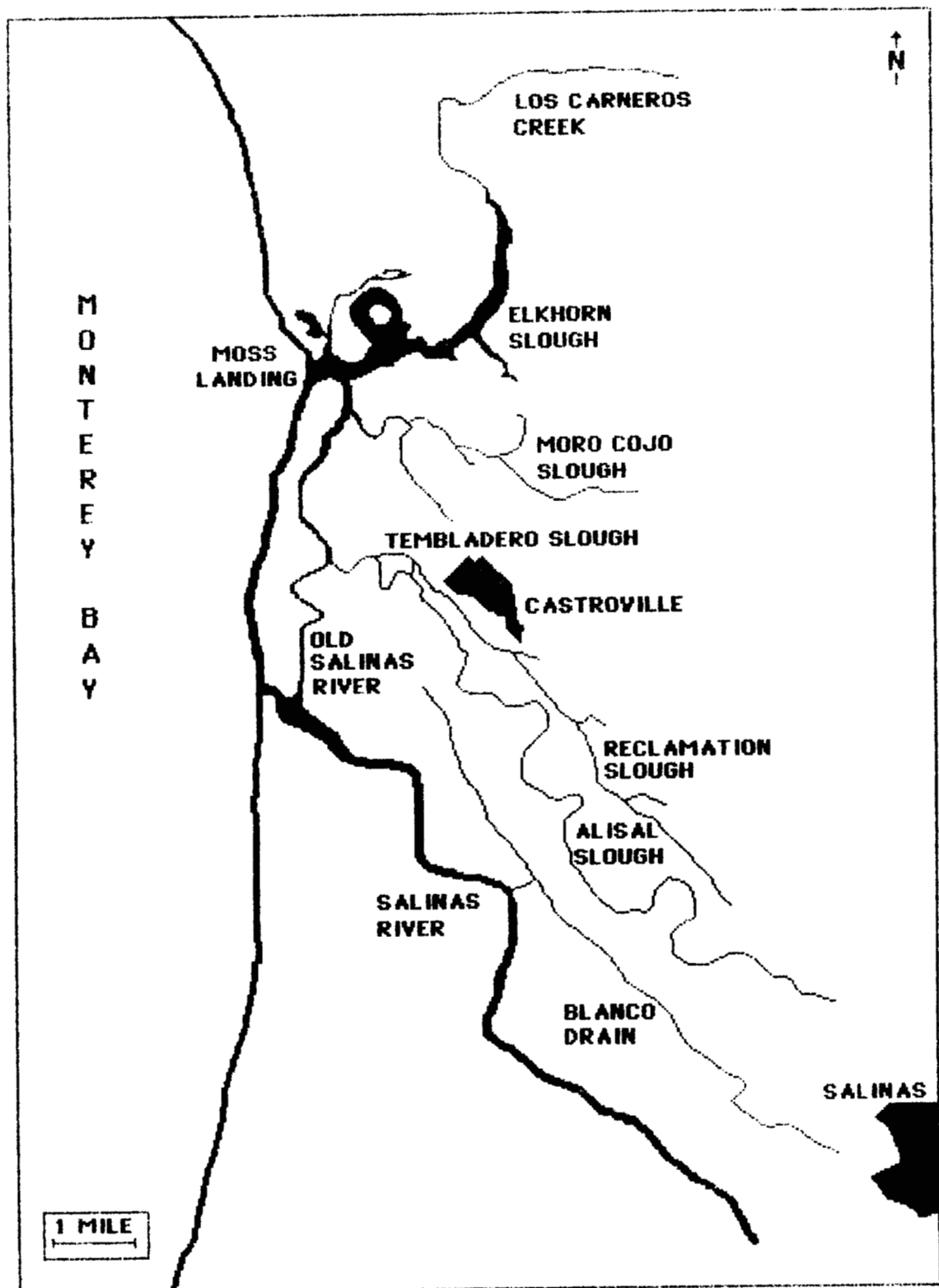


Figure 1. Moss Landing Drainage area of Monterey County, California.

Endosulfan residues have consistently been detected in Elkhorn Slough by the California State Mussel Watch Program (SMWP) since 1979 (Phillips 1988, State Water Resources Control Board 1988, 1989). The SMWP uses bivalve organisms as bio-indicators of pollutant exposure in coastal regions of the State. Since 1979, SMW collected 48 samples from 13 locations in the Moss Landing area, all of which contained endosulfan residues. Endosulfan concentrations in mussels from this region are frequently higher than in any other coastal area of California (Phillips 1988).

There is not a great deal of information on endosulfan levels in surface waters of the Moss Landing drainage area (Ross 1990). Endosulfan has not been detected consistently in surface water of this region in prior studies (Coleman and Dolinger 1978, Gonzalez et al., 1987). Movement of endosulfan from target areas into surface waters of this region was only evidenced indirectly by the consistent detection of endosulfan in aquatic organisms, which tend to bio-accumulate this compound. Due to the lack of information concerning the mechanism of off-target movement in this area, this study was conducted to determine if endosulfan moves off-target via spray drift and/or rain runoff. Results from this investigation could then be used by regulatory personnel to determine if mitigation measures are feasible.

MATERIALS AND METHODS

Study Area

Three artichoke fields in the Moss Landing drainage area were selected for this study. Fields 1, 2, and 3 were similar in size (12.1, 9.3, and 12.1 ha), drained into Tembladero Slough, and were scheduled for fall 1988 applications of endosulfan. Soils were classified as a Diablo clay, Pacheco clay loam, and Clear Lake clay for fields 1, 2, and 3, respectively (USDA 1978).

The applications, which began about 0630 and ended around 0800, occurred on Nov. 17, 15, and 16, 1988, on fields 1, 2, and 3, respectively. Prior endosulfan applications occurred on March 5, 1988, Feb. 24, 1988, and

greater than 10 months before application, respectively. Each application mixture consisted of Thiodan® EC (the formulated product of endosulfan) at 2.9 L/ha (1.05 kg/ha active ingredient), Phosdrin® (2.3 L/ha), Triton CS-F Spreader (140 g/ha) and water (93.5 L/ha). Applications were performed using a Bell G-5-45 helicopter equipped with a 12.2 m (40-foot) spray boom operated at 1.4 to 1.7×10^5 Pa (20 to 25 psi).

Meteorological data including wind speed and direction, air temperature and precipitation were collected from a local CIMIS (California Irrigation Management Information System) station operating in Castroville, within 1.6 km of each field.

Sample Collection

The deposition of endosulfan on- and off-target was measured using fall-out sheets (consisting of plastic-backed absorbent paper), 0.0929 m^2 in area. Ten fallout sheets were randomly placed on-target along a diagonal laid out across each field. An additional 16, used to measure off-target deposition, were placed around each field at a distance of 5.5 m from the field borders.

Soil samples were collected from each field prior to and immediately following endosulfan application. Eight composite samples, consisting of five randomly selected subsamples, were collected using a stainless steel tube, 5.9 cm in diameter, inserted 5 cm deep. Eight composite samples were also randomly taken from soil of collector drains located at the edge of each field before and after application. These drains were not sprayed during application and served to channel water off-target. During sampling, collector drains were dry yet they typically contain moving water after rain or irrigation events. All soil samples were placed in glass jars, capped with aluminum-lined lids, weighed, and placed on dry ice.

Rain runoff samples were collected from one drain pipe per field, even though most fields had more than one drain pipe. Field 1 had a total of six drains, field 2 had three and field 3 had only one. These fields all drained either directly or indirectly into Tembladero Slough, which empties into the Old Salinas River (Figure 1). Unfiltered runoff samples

were collected in one gallon glass bottles, capped with aluminum-lined lids, and stored at 4°C until analyzed. Water temperature, pH, and flow rate of runoff water were recorded at the time of sampling.

Chemical Analysis

Fallout Samples

Fallout sheets were extracted with 500 mL of ethyl acetate by shaking for 45 min. Where necessary, an aliquot of the sample was first diluted from 1 mL to 10 mL with ethyl acetate, then analyzed for endosulfan I, II and sulfate by gas chromatography (GC) using a Hewlett Packard (HP) 5880A equipped with a ⁶³Ni electron-capture detector and a 12-m capillary column (HP-1). The carrier gas (high purity helium) flow rate was 1.5 mL/min with a split vent at 50 mL/min, septum purge of 2 mL/min, and make-up gas flow of 30 mL/min. Column, injector, and detector temperatures were 220, 250, and 350°C, respectively (Appendix I). Samples were extracted and analyzed within 7 weeks of collection. The minimum detection limit (MDL) for each of the endosulfans on fallout sheets was 10 ug per sample.

Soil Samples

Soil (50 g) was extracted by shaking with 150 ml of a hexane:acetone (50:50) mixture for 1 h. The extract was filtered through 50 g of sodium sulfate into a 500-ml round-bottom flask. The extraction procedure was repeated once more and the filtered extracts combined. An additional 60 ml of hexane:acetone (50:50) was used to rinse the extraction vessel and filter and added to the round-bottom flask. The extract was evaporated to near dryness on a rotary evaporator at 45°C, transferred to a graduated tube using 10 ml of hexane, and concentrated to a final volume of 4 ml under nitrogen. Sample clean up was then conducted using a florisil column (see Appendix I for details). The sample was analyzed with a Varian 6000 GC, equipped with an electron capture detector and a 10 m megabore column (HP-5). The column temperature was 200°C (held for 12 min), injector and detector temperatures were 210 and 250°C, respectively. Samples were extracted within four months and analyzed within five months of collection. The MDL for each of the endosulfans was 4 ug/kg, dry weight.

Water Samples

Whole water samples (1 L, unfiltered water) was extracted by shaking with 100 ml of methylene chloride for 2 min (Appendix I). The layers were allowed to separate and the organic portion was filtered through sodium sulfate and collected in a 500-ml boiling flask. The extraction was repeated twice using 80 ml of methylene chloride. The sodium sulfate was rinsed with 20 ml of methylene chloride and collected in the same flask. The extract was taken to dryness on a rotary evaporator at 40°C. The sample was transferred with 10 ml hexane to a tube and evaporated to a final volume of 1 ml with a gentle stream of nitrogen. Samples were analyzed with a Varian 3700 GC equipped with a Hall detector and a crosslinked (50% Ph Me Si) column (HP-17). Column, injector, and detector temperatures were 220, 210, and 250°C, respectively. Samples were extracted and analyzed within one month of collection. The MDL for each of the endosulfans was 0.10 ug/l.

RESULTS AND DISCUSSION

Deposition On-target

Deposition on-site for the three fields averaged 1.13 kg/ha (endosulfan I plus II), similar to the intended rate of 1.05 kg/ha (Table 1). Endosulfan sulfate was not detected in fallout samples as expected since the formulated product contains endosulfan I and II only. Also, the ratio of I to II on fallout sheets was similar to the theoretical ratio of 2:1 (Table 1). The range in on-site deposition was 0.93 to 1.48 kg/ha, with the lowest application reported on field 3. Wind speeds were higher during this application (Table 2) and might have influenced deposition rates.

Eighty-nine to 140% of the intended application rate was actually measured on the three fields. Reports of deposition being higher than intended rates have been seen previously during the eradication project for Mediterranean fruit fly (Segawa 1991), where helicopters were also used for application. Generally, application efficiencies for fixed-wing

Table 1. Deposition of endosulfan on fallout cards placed on- and off-target on three artichoke fields in Monterey County, California.

On-target Deposition

<u>Application</u>	<u>Field</u>	<u>n</u>	<u>Mean Endosulfan Deposition^a</u>		
			<u>I</u>	<u>II</u>	<u>Total</u>
			----- kg/ha -----		
11/17/88	1	5	0.93(0.36) ^b	0.54(0.25)	1.48(0.61)
11/15/88	2	10	0.59(0.30)	0.38(0.21)	0.97(0.51)
11/16/88	3	10	0.58(0.33)	0.35(0.21)	0.93(0.54)
Mean of three fields		3	0.74(0.18)	0.43(0.10)	1.13(0.30)

Off-target Deposition

<u>Application</u>	<u>Field</u>	<u>n</u>	<u>Mean Endosulfan Deposition^a</u>		
			<u>I</u>	<u>II</u>	<u>Total</u>
			----- kg/ha -----		
	1	16	0.011(0.011)	0.005(0.006)	0.016(0.017)
	2	16	0.012(0.014)	0.007(0.008)	0.019(0.022)
	3	17 ^c	0.003(0.004)	0.001(0.002)	0.005(0.006)
Mean of three fields		3	0.009(0.005)	0.004(0.003)	0.013(0.007)

a. I = endosulfan I, II = endosulfan II. Endosulfan sulfate was not detected (detection limit was 10 ug per sample).

b. Standard deviation in parentheses.

c. An additional sample was collected.

Table 2. Meteorological data from the California Irrigation Management Information System (CIMIS) in Castroville, California, 1988. Data shown for the hours of endosulfan application only.

<u>Date</u>	<u>Hour</u>	<u>Speed</u>	<u>Direction</u> ^a	<u>Temperature</u>
		-- m/s --	-- degrees --	-- °C --
11/17	0600	1.83	329	12
(field 1)	0700	1.61	143	12
	0800	1.07	224	12
11/15	0600	0.80	77	12
(field 2)	0700	0.94	167	12
	0800	1.34	115	12
11/16	0600	2.37	145	12
(field 3)	0700	3.04	151	12
	0800	3.04	152	12

a. For wind direction, 0 or 360° = north.

aircraft range between 5 and 85% of intended rates (Miller 1980, Ross and Sava 1986).

Deposition Off-target

Endosulfan residues were detected off-target at all three fields. Average off-target endosulfan concentrations ranged from 0.005 to 0.019 kg/ha (Table 1). This represents roughly 0.4 to 1.8% of the intended application rate and 0.5 to 2.0% of measured rates. Deposition of pesticides off-target will vary depending on meteorological conditions at the time of application. Field 3 had the lowest off-target (as well as on-site) deposition and the highest wind speeds during application (Table 2). Higher wind speeds will generally cause a decrease in atmospheric concentrations downwind of a source due to dilution (Wark and Warner 1981). In terms of deposition, higher wind speeds may tend to disperse residues further off-target, thereby reducing deposition near the source.

Soil, On-target

Pre-application concentrations of total endosulfan (I + II + sulfate) in soil taken on-site averaged 2.3, 1.5, and 0.8 mg/kg, dry weight, in fields 1, 2, and 3, respectively (Table 3). Prior endosulfan applications occurred 8, 9, and greater than 10 months before soil sampling on fields 1, 2, and 3, respectively. Field 3 had the lowest residues of total endosulfan perhaps reflecting the amount of time since last application. Both endosulfan I and II degrade to sulfate, partially explaining the predominance of sulfate in field soil. In addition, half-life estimates for endosulfan have been reported as 60 days, 800 days and several years for I, II, and sulfate, respectively (Stewart and Cairns 1974). In all cases, pre-application concentrations reflect the degradation pattern and longevity of these compounds in soil with sulfate residues greater than endosulfan II, which were greater than endosulfan I (Table 3).

Post-application concentrations of total endosulfan averaged 3.7, 3.0, and 2.1 mg/kg, dry weight, on fields 1, 2, and 3, respectively (Table 3). The increase in endosulfan concentrations over pre-application levels came in the form of endosulfan I and II, as anticipated, given the formulated product composition.

Table 3. Endosulfan concentrations in soil collected from artichoke fields in Monterey County, California. Soil samples were collected on-target and from collector drains off-target in addition to pre- and post-application.

On-target

Application	Field	Mean Endosulfan Concentration ^a			
		I	II	Sulfate	Total ^b
		----- ug/kg, dry weight -----			
pre	1	48(56)	521(126)	1785(361)	2287(489)
post	1	835(472)	1098(294)	1856(490)	3719(801)
pre	2	23(14)	426(94)	1144(277)	1549(355)
post	2	1013(513)	1020(343)	1041(122)	3034(816)
pre	3	22(14)	274(57)	531(128)	807(158)
post	3	776(528)	836(331)	542(177)	2134(733)

Collector Drains Off-target

Application	Field	Mean Endosulfan Concentration ^a			
		I	II	Sulfate	Total ^b
		----- ug/kg, dry weight -----			
pre	1	57(15)	436(121)	1121(386)	1572(488)
post	1	234(155)	528(242)	1088(366)	1808(724)
pre	2	21(19)	261(88)	574(136)	834(211)
post	2	111(85)	453(144)	891(337)	1421(507)
pre	3	15(12)	195(76)	366(66)	562(137)
post	3	18(11)	150(61)	318(88)	473(75)

a. Mean (standard deviation in parentheses) of 8 samples. To calculate means where values were none detected (detection limit = 4 ug/kg), the value was set at 2 ug/kg (one half the detection limit).

b. Total endosulfan = endosulfan I + II + (0.96217 x sulfate). The weighting factor for endosulfan sulfate accounts for the difference in molecular weight between sulfate and the I and II isomers.

Similar soil results were seen in artichoke fields of this region in another study (Oakden and Oliver, 1988). Pre- and post-application concentrations of total endosulfan were 1.3 and 3.2 mg/kg dry weight, respectively. The distribution of endosulfan I, II and sulfate in all soil samples was also similar, with sulfate concentrations highest, followed by II and I.

Soil, Off-target

Pre-application concentrations of total endosulfan from collector-drain soil were lower than those found on site. Average soil concentrations of total endosulfan were 1.6, 0.83, and 0.56 mg/kg, dry weight, in collector drains of fields 1, 2, and 3, respectively (Table 3). Similar observations have been noted before in this area (Oakden and Oliver 1988) and other areas of North America (Miles and Harris 1971, Braun and Frank 1980). It has been suggested that the difference between soil concentrations on field and in agricultural drains indicates that drains are not serving as a sink for endosulfan (Oakden and Oliver 1988). In that study the authors implied that these residues move further off-target, eventually into Monterey Bay.

Post-application concentrations averaged 1.8, 1.4, and 0.47 mg/kg, dry weight, in drains of fields 1, 2, and 3, respectively. Post-application concentrations in collector drains of fields 1 and 2 were not a great deal larger than pre-application concentrations. However post-application concentrations found in the collector drain of field 3 were about the same as pre-application concentrations. Weather plays a major role in deposition of residues off-target (Lee 1976). As an example, field 3 had higher wind speeds at the time of application and lower post-application concentrations than the other fields. With higher wind speeds and more turbulent conditions atmospheric pollutants tend to be dispersed further from the source (Lee 1976).

Rain Runoff

The first rain event monitored on November 23, 1988, produced 9 mm of rain, and generated runoff on field 1 only (Table 4). The second event monitored on December 22, 1988, produced 8 mm of rain, and generated

Table 4. Endosulfan concentrations in rain runoff collected from artichoke fields in Monterey County, California.

Date	Field	Time	Flow	Mean Endosulfan Concentrations			
				I	II	Sulfate	Total ^a
			--l/min--	----- ug/l -----			
11/23	1	1445	1.89	1.21(0.43) ^b	3.69(1.18)	8.82(3.03)	13.38(4.34)
11/23	1	1615	3.79	0.93(0.20)	2.25(1.38)	7.30(1.08)	10.21(2.45)
12/22	1	1400	2.08	0.39(0.02)	1.34(0.14)	5.04(0.30)	6.59(0.22)
12/22	1	1815	0.95	0.74(0.18)	1.20(0.26)	4.66(2.05)	6.43(2.24)
12/22	2	1645	1.89	0.43(0.09)	0.96(0.07)	3.14(0.22)	4.41(0.35)
12/22	3	1500	0.64	0.28 ^c	0.44	1.50	2.16

a. Total endosulfan = endosulfan I + II + (0.96217 x sulfate). The weighting factor for endosulfan sulfate accounts for the difference in molecular weight between sulfate and the I and II isomers.

b. Means calculated from 3 samples which were collected during each sampling interval. Standard deviation appears in parentheses.

c. Only one sample was collected because runoff ceased.

runoff from all three fields (Table 4). Only partial runoff volumes from each of the three fields are available. Runoff was sampled only once or twice from each field during each runoff event due to the distance between field sites and the Sacramento office. In addition, only one drain pipe per field was sampled during runoff since the objective of the study was simply to document if endosulfan moves off-target in runoff water.

All three forms of endosulfan were detected in each sample (Table 4) demonstrating that this material moves off-target in rain runoff in this region. In all cases, runoff concentrations of endosulfan sulfate were greater than endosulfan II which were greater than I, reflecting their relative concentrations in soil. In terms of relative solubility of the endosulfans, endosulfan II and sulfate may be slightly less soluble than endosulfan I. Solubilities measured by Bowman and Sans (1983) were 0.51, 0.45 and 0.48 mg/L for endosulfan I, II, and sulfate, respectively. Other measurements reported by Callahan et al. (1979) were 0.53, 0.28, and 0.22 mg/L, respectively. Since concentrations of endosulfan sulfate were at least two times higher than concentrations of II, which in turn were twice as high as I, their relative solubilities can not explain these results.

Endosulfan can be transported in dissolved form as well as attached to soil particles. According to Willis et al. (1987) about 40% of the endosulfan (I and II only) transported in a Mississippi watershed was attached to suspended sediment, the remainder was in dissolved form. Therefore concentrations of endosulfan in agricultural runoff could be influenced by the amount of soil carried in runoff water. This in turn implies that the relative concentrations of endosulfan in rain runoff may be dependent on soil erosion and soil half-lives.

Since endosulfan is transported in watersheds attached to soil (Willis et al. 1987), soil adsorption might also play a role in resultant runoff concentrations. Endosulfan I and II have high soil adsorption values where the K_{oc} ranges from 8×10^3 to 21×10^3 ml/g for endosulfan I, and 9×10^3 to 14×10^3 ml/g for endosulfan II (Hoechst 1987). Soil adsorption of endosulfan sulfate has not been measured. The absence of: (1) direct measurements of total endosulfan on suspended sediment and (2) adsorption values for sulfate, precludes the determination of the predominant phase of endosulfan in runoff water of this study.

Concentrations of total endosulfan in rain runoff ranged from 2.2 to 13 ug/L. These concentrations are well above the instantaneous water quality criterion of 0.22 ug/L. Without sufficient dilution, coupled with multiple sources in a single watershed, these runoff concentrations could adversely affect water quality.

Other studies have also demonstrated that endosulfan moves off-target in runoff water. Miles and Harris (1971) and Braun and Frank (1980) detected residues of endosulfan in agricultural watersheds of Ontario, Canada. Spencer et al. (1985) detected between 0.4 and 71 ug/L of endosulfan in irrigation runoff water sampled at field sites in Imperial County, California. Rain runoff concentrations in this study fall on the lower end of that range. Run-off concentrations will vary and depend on many factors including: rain-storm intensity and duration, time between application and storm event (although this is less of a factor with the organochlorines since they are typically long lived), and soil slope and type (Wauchope 1978).

Certain cultural practices used in artichoke farming facilitate water runoff from artichoke fields. Roots of artichoke plants are sensitive to moisture therefore water drainage is maximized by "V" ditches: 2-foot deep, steep-sided ditches placed between plant rows. These "V" ditches then drain into collector drains at the fields' edge. In addition, vegetation is periodically removed from the "V" ditches with ground applied herbicides, leaving bare soil exposed. Without ground cover to stabilize the soil, erosion is more likely to occur, taking with it any soil adsorbed endosulfan. Also, aerial applications potentially increase the mass of endosulfan available for runoff since the pesticide is not directed onto target crops as in ground applications.

CONCLUSIONS

Results from this study indicate that endosulfan moves off-target via drift and rain runoff from artichoke fields sampled in the Moss Landing drainage area. It should be noted however, that the relative magnitude of drift and runoff losses depends on a variety of environmental parameters including atmospheric conditions, soil type and texture, precipitation

patterns and cultural practices. Even though results in this study do not lend themselves to interpretation of the relative contribution of these two transport mechanisms, the study does demonstrate that endosulfan moves off-target in both spray drift and in rain runoff in Monterey County. These results are consistent with studies conducted in other areas of North America.

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A P P E N D I X I

C H E M I C A L A N A L Y S E S

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Original Date: 11/19/88
Supercedes: NEW
Current Date: 4/11/91
Method #:

CHEMICAL ANALYSIS OF ENDOSULFAN I AND II FROM KIMBIES™

SCOPE:

This method is for the determination of Endosulfan I and II on Kimbie™ cards.

PRINCIPLE:

Residues of endosulfan I and II were extracted from Kimbies™ (absorbant towel with a plastic backing) by shaking with ethyl acetate. Residue levels of endosulfan in milligram amounts were diluted (1 mL to 10 mL). Analysis was performed by gas chromatography using a Ni⁶³ electron-capture detector.

REAGENTS AND EQUIPMENT:

Ethyl acetate; (pesticide residue grade).
Wide-mouth mason jars (quart size).
Mechanical shaker (G10 Gyrotory Shaker).
Graduate test tubes (15 mL).
Nitrogen evaporator (Organomation Model # 12).
Vibrating mixer for test tubes.
Graduated cylinder (1 L).
Kimbie™ (Kimberly-Clark Corp).

ANALYSIS:

- 1) Place the Kimbie™ in a quart mason jar. Add 500 mL of ethyl acetate and shake on a mechanical shaker for 45 minutes at a setting of ~ 165 RPM.
- 2) Take 1 mL aliquot of the initial ethyl acetate extract and dilute 1:10 with ethyl acetate. Submit sample for gas chromatographic analysis.

EQUIPMENT CONDITIONS:

ENDOSULFAN I AND II

Hewlett Packard (HP) 5880A GC WITH ECD
Column: HP-1 (100% methyl silicone) 12 m x 0.20 mm x 0.33 um
Carrier gas: Helium, flow rate: 1.5 mL/minute. (20 psi).
Split vent: 50 mL/minute.
Septum purge: 2 mL/minute.
Make-up gas: Argon-Methane (95:5%), flow rate: 30 mL/minute.
Injector: 250°C.
Detector: 350°C.
Oven Temperature: 220°C isothermal.
Injection volume: 2 uL.

EQUIPMENT CONDITIONS: continued

Retention times: Endosulfan I - 2.80 ± 0.05 minutes
 Endosulfan II - 3.60 ± 0.05 minutes

Linearity check: 0.01ng - 2ng.

CALCULATIONS:

Micrograms (UG) ENDOSULAN I AND II

$$\text{ug in sample} = \frac{(\text{peak height sample})(\text{ng/UL std})(\text{UL injected std})(\text{final volume mLs})}{(\text{peak height std})(\text{UL injected sample})(500 \text{ mL})}$$

FORTIFICATION:

Endosulfan I and II were spiked onto separate Kimbie™ sheets at the levels listed below. The Kimbies™ were allowed to dry before extraction.

RECOVERIES:

% Recoveries of Endosulfan I and II blank matrix spikes: Kimbie™.

Analyte: Endosulfan I
 Detection limit: 10 ug

LAB Sample #	Results (mg)	Spike level (mg)	Recovery %	\bar{X}	SD	CV (%)
5869	4.66	5	93.1			
5870	4.81	5	96.1			
5871	4.93	5	98.7			
5872	4.70	5	94.0			
5873	4.58	5	91.5	94.7	2.79	2.95

Analyte: Endosulfan II
 Detection limit: 10 ug

LAB Sample #	Results (mg)	Spike level (mg)	Recovery %	\bar{X}	SD	CV (%)
5869	4.52	5	90.4			
5870	5.00	5	100			
5871	5.22	5	104.4			
5872	5.00	5	100			
5873	4.82	5	96.3	98.2	5.23	5.33

RECOVERIES: continued

Recovery validation was done prior to analysis.

DISCUSSION:

Each run contained standards of 0.01 ng/uL, 0.1 ng/uL, and 1 ng/uL at the begining, end, and after every 15 samples. Samples with higher residues were diluted and reanalyzed with 10 ng/uL standards. A blank and 10 ug level spike were analyzed with each set of samples.

REFERENCE:

- 1) White, Jane, *Parathion on Kimbies*, 1989 Environmental Monitoring Methods, California Department of Food and Agriculture.

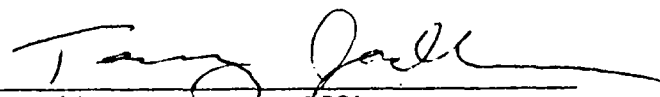
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Original Date:
Superceeds: New
Current Date:
Method #

ENDOSULFAN

SCOPE:

This method has been developed and used for the analysis of the alpha, beta, and sulfate forms of endosulfan in soil.

PRINCIPLE:

The alpha, beta, and sulfate forms of Endosulfan are extracted with a hexane:acetone mixture. The extract is concentrated to a final volume in hexane. A portion of the extract is transferred to a florisil column. After washing the column with a 3% diethyl ether:hexane solution, the compounds are eluted from the column with a 50% diethyl ether:hexane solution.

REAGENT AND EQUIPMENT:

- 1) Solvents: hexane, pesticide grade.
acetone, pesticide grade.
ethyl ether, pesticide grade.
ethanol, pesticide grade.
- 2) Sodium sulfate, anhydrous.
- 3) Chromatographic column (11mm x 300mm) - Kimble #17810-11300
- 4) Glasswool.
- 5) Filter paper - Whatman #1.
- 6) Activated florisil (overnight at 130°C).
- 7) Brown bottle (500ml) Qoropak[®].
- 8) Drying oven.
- 9) Mechanical shaker - G-10 Gyrotory (R) Shaker
- 10) Flask, flat-bottom boiling, 250mL and 500mL
- 11) N-EVAP[®], Analytical nitrogen evaporator
- 12) Ottawa sand standard: (20-30 mesh) - Fisher Scientific Co.

ANALYSIS:

MOISTURE DETERMINATION

- 1) Mix the soil sample in its container using a spoon to achieve a uniform mixture.
- 2) Weigh approximately 15-20 g of soil into a preweighed aluminum weighing pan.
- 3) Place the aluminum pan containing the soil sample in a 105°C oven overnight.
- 4) Place the pan into a dessicator to cool to ambient temperature (~1-2 hours). Make sure the weight of the pan remains constant in subsequent weighings calculating the percent moisture.

SAMPLE EXTRACTION

- 1) Weight 50g of soil into a 500ml brown bottle.
- 2) Add 150mL hexane:acetone (50:50) mixture to the bottle and shake the bottle for one hour at 220 rpm.
- 3) Pour the extract from the bottle through a funnel containing filter paper and 50g sodium sulfate into a 500mL round bottom flask.
- 4) Repeat step #2 using 100mL of the hexane:acetone(50:50)mixture. Shake the bottle for 30minutes at 220 rpm.
- 5) Transfer the extract into the same 500mL flask. Rinse the bottle and the funnel a few times with a total of 60mL of hexane:acetone (50:50) mixture.
- 6) Evaporate the extract to near dryness on a rotary evaporator at 45 °C and 15 inches of vacuum.
- 7) Transfer the extract to a graduated test tube using 10mL of hexane.
- 8) Concentrate the extract to a final volume of 4mL hexane under nitrogen on the N-EVAP[®].

SAMPLE CLEAN UP

- 1) Prepare a florisil column as follows: after a small amount of glasswool has been added to the bottom of the column, fill the column with hexane, add 15mL of activated florisil. Tap the column to eliminate any air. Add about 5g of sodium sulfate or sand to protect the column.
- 2) Prepare the elution Mixture I (3% diethyl ether:hexane) as follows: 30mL diethyl ether * is diluted to 1L with hexane and 10grams of anhydrous sodium sulfate is added to remove any water.
*** The diethyl ether must contain 2% (v/v) anhydrous ethanol and must be free of peroxides.**
- 3) Prepare the elution Mixture II () as follows:
* 500mL diethyl ether is diluted to 1L with hexane and 10grams of anhydrous sodium sulfate is added to remove any water.
- 4) Transfer a 2mL aliquot from the 4mL sample to the top of a prepared florisil column.
- 5) Wash the column with 50mL hexane at the flow rate about 3ml/min. Discard the eluate.
- 6) Wash the florisil column with 75mL of the elution Mixture I at the flow rate about 3ml/min. Discard the eluate.

- 7) Add 150mL of the elution Mixture II to the florisil column . Collect the eluate in a 250mL flat bottom flask at the flow rate about 3ml/min. Reduce the volume to 1-2ml using a rotary evaporator. Transfer the extract to the graduated test tube using about 10ml of hexane.
- 8) Reduce the volume to 2mL on the nitrogen evaporator.
- 9) Send the sample for GC analysis.

EQUIPMENT AND CONDITION:

- 1) Varian 6000 with Electron Capture Detector.
 Column HP-5 (5% methyl silicone).Megabore
 10m x2.0um film thickness.
 Temperature: Isothermal 200°C held for 12 min .
 Injector: 210°C
 Detector: 250°C.
- 2) Confirmation: Varian 6000 and 3700 with Electrolytic Conductivity Detector, in Halogen mode.

 Column H-P 17 megabore ,10m x 2.0um film thickness.
 Injector: 220°C
 Detector: 250°C
 Column Temperature: Isothermal 220°C held
 for 10 min.

CALCULATION:

All results should be reported by ppm dry weight.

$$\text{PPM(wet)} = \frac{\text{Final vol. (uL)} \times \text{Amount of std (ng)} \times \text{Peak height of sample} \times 1,000}{\text{Volume of sample injected (uL)} \times \text{sample weight (g)} \times \text{peak height of std}}$$

$$\text{PPM(dry)} = \frac{\text{PPM(wet)}}{1 - \text{moisture}}$$

$$\text{Moisture} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Wet weight}}$$

DISCUSSION:

SENSITIVITY :

The minimum detection limit for thiodan I,II, and Sulfate is 4ppb .

RECOVERIES :

Endosulfan I :

40 ppb : Mean = 77.1 % , n = 5 , Standard deviation = 3.4
 400 ppb: Mean = 87.1 % , n = 5 , Standard deviation = 5.1

Endosulfan II :

40 ppb : Mean = 104.5 % , n = 5 , Standard deviation = 5.6

400 ppb: Mean = 96.0 % , n = 5 , Standard deviation = 3.2

Endosulfan sulfate :

40 ppb : Mean = 124.1% , n = 5 , Standard deviation = 8.9

400 ppb: Mean = 106.7% , n = 5 , Standard deviation = 3.0

The provided background soil was used for the above spikes and the amounts of endosulfan I,II, and sulfate in the background soil were:

Endosulfan I: Mean = 6.0 ppb , n = 5 , Standard deviation = 1.0

EndosulfanII: Mean = 18.5ppb , n = 5 , Standard deviation = 2.1

Endosulfan sulfate: Mean =19.7ppb , n = 5 ,Stand. deviation = 2.5

REFERENCES:

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Original Date: 06/28/89
Supercedes: New
Current Date: ??
Method #:

THIODAN I, II & III IN RAIN-WATER RUNOFF

SCOPE:

This method is for the determination of thiodan I, II & III in rain water runoff.

PRINCIPLE:

The samples of rain-water runoff were extracted by shaking in a separatory funnel with methylene chloride. The extract was filtered and evaporated to dryness. It was then transferred and brought up to final volume with hexane. The extract was analyzed by gas chromatograph using a Hall detector.

REAGENTS AND EQUIPMENT:

- 1) Solvent; (pesticide residue grade) methylene chloride and hexane.
- 2) Sodium sulfate (anhydrous).
- 3) Separatory funnel (2 liter).
- 4) Boiling flasks, flat bottomed (500ml).
- 5) Glass stem funnels.
- 6) buchner funnels (large).
- 7) suction flask (1 liter).
- 8) Filter paper (MSI nylon, plain 0.45 micron, 142mm).
- 9) Rotary evaporator (Buchi/Brinkmann, R110).
- 10) Graduate test tubes (15ml).
- 11) Nitrogen evaporator (Organomation Model #12).
- 12) Varian 3700 gas chromatograph with hall detector.

ANALYSIS:

- 1) Remove sample from refrigerated storage and allow them to come to room temperature.

- 2) Shake sample well. Measure out 1 liter and transfer to a 2 liter separatory funnel. Extract sample by shaking with 100 ml of methylene chloride for 2 min..
- 3) Allow layers to separate and filter the organic layer through sodium sulfate. Collect extract in a 500 ml boiling flask.
- 4) Repeat extraction two more times using 80 ml of methylene chloride.
- 5) Rinse sodium sulfate with 20 ml methylene chloride and collect in the same 500 ml boiling flask.
- 6) Take extract just to dryness on a rotary evaporator at 40° C
- 7) Transfer sample with 10 ml hexane to a test tube and evaporate to a final volume of 1 ml with a gentle stream of nitrogen. Submit sample to gas chromatograph for analysis.
- 8) For quality assurance check a 10 ppb spike of thiodan I, II & III was added to a liter of each sample and steps 1-7 were followed.

Sediment Analysis:

- 1) Weight of filter paper recorded.
- 2) Take a liter of each sample and filter using a Buchner funnel and suction flask.
- 3) The sediment and filter paper were allowed to dry at room temperature.
- 4) Record weight of sediment and filter paper.

EQUIPMENT CONDITIONS:

VARIAN 3700 G.C. WITH HALL DETECTOR
 COLUMN: HP-17 (Crosslinked 50% Ph Me Si) 10m x 0.53mm x 2.0um film thickness.
 CARRIER GAS: Helium
 INJECTOR: 210° C, DETECTOR: 250° C;
 TEMPERATURE: 220° C

CALCULATION:

PPB THIODAN I, II and III

$$\frac{(\text{peak height sample}) \times (\text{ng std}) \times (\text{final volume mls}) \times 1000}{(\text{peak height std.}) \times (\text{ul sample injected}) \times (\text{volume of sample})}$$

RECOVERIES:

Recoveries of thiodan I, II and III at these levels:

Levels	Thiodan I	Thiodan II	Thiodan III
0.3ppb	97-113%	97-110%	90-110%
1.0ppb	71-107%	83-121%	80-133%
10.0ppb	100-120%	94-117%	111-123%
50.0ppb	102-107%	100-103%	97-107%
250.0ppb	96-107%	102-105%	102-110%

SENSITIVITY:

0.4ng thiodan I ~ 60% of full scale

0.4ng thiodan II ~ 40% of full scale

0.4ng thiodan III ~ 20% of full scale

MINIMUM DETECTABLE LEVEL:

0.1ppb (1 liter volume of sample used).

DISCUSSION:

The sediment contents varied between samples. The amount of sediment in each was determined by filtration. A portion of each sample was spiked with 10 ppb of thiodan I, II and III to check for recovery levels. The recovery levels were low for the spike and could be due to the sediment in the sample.

REFEENCE:

- 1) "The Sampling and Analysis of Water for Pesticides", EPA Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples, Sect. 10, A, pg 1-8, 1979.

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